

BULK SUPERHARD B-C-N NANOCOMPOSITE COMPACT AND METHOD FOR
PREPARING THEREOF

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STATEMENT REGARDING FEDERAL RIGHTS

This invention was made with government support under Contract No. W-7405-ENG-36 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

FIELD OF THE INVENTION

10 The present invention relates generally superhard materials and more particularly to a superhard compact of nanocrystalline grains of at least one high-pressure phase of B-C-N embedded in a diamond-like amorphous carbon matrix and to a method for preparing the superhard compact.

BACKGROUND OF THE INVENTION

15 Superhard materials have a Vickers hardness (H_V), i.e. an indentation hardness, of at least 40 GPa and are widely used as abrasives for drilling, cutting, and other machining applications. Superhard materials often include boron, carbon, nitrogen and oxygen because these light elements have a small atomic radius and form strong and directional covalent bonds that produce tight, three-dimensional networks with extreme resistance to external shear.

20 Diamond is the hardest superhard material currently known, with an H_V of about 70-100 GPa. However, the actual performance of diamond as an abrasive is somewhat limited. Diamond is an unsuitable abrasive for machining ferrous alloys and has limited applications for high-speed cutting because it is converted 25 into graphite in the presence of oxygen at temperatures over 800 °C.

Cubic BN (cBN) is another important superhard material. While cBN is widely used for machining fully hardened steels and exhibits much better thermal stability than diamond, it is only about half as hard ($H_V=45\sim50$ GPa) as diamond.

Superhard materials for industrial use are often in the form of sintered polycrystalline composites that incorporate microcrystalline grains of diamond or cubic boron nitride. The grains of this composite are tens to hundreds of micrometers in size, and usually include vacancies, dislocations, and other 5 imperfections that multiply and propagate to form microcracks within individual crystals of a grain, and also along grain boundaries. As the microcracks grow, the materials deform and fracture.

Recently, a new class of materials known as superhard nanocomposites has been reported. Superhard nanocomposites contain superhard nanocrystalline 10 grains embedded in an amorphous matrix. The amorphous matrix provides amorphous grain boundaries that absorb vacancies and dislocations, reduces the surface energy and residual stress among the grains, and permits the relaxation of mismatches between adjacent grains of different phases. While a number of superhard nanocomposites have been reported, no superhard nanocomposite 15 bulk compact having the Vickers hardness of diamond has yet been prepared. Thus, there remains a need for a superhard nanocomposite compact with improved hardness, strength, and performance.

Therefore, an object of the present invention is to provide a bulk superhard nanocomposite compact with a high Vickers hardness.

20 Another object of the invention is to provide a method for preparing a bulk superhard nanocomposite compact with a high Vickers hardness.

Additional objects, advantages and novel features of the invention will be 25 set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

SUMMARY OF THE INVENTION

In accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention includes a superhard nanocomposite compact. The compact consists essentially of nanocrystalline grains of at least one high-pressure phase of B-C-N surrounded by amorphous diamond-like carbon grain boundaries.

The invention also includes a process for preparing a bulk superhard nanocomposite compact consisting essentially of nanocrystalline grains of at least one high-pressure phase of B-C-N surrounded by amorphous, diamond-like grain boundaries. To prepare the compact, a mixture of graphite and hexagonal boron nitride is ball-milled. The ball-milled mixture contains amorphous and/or nanocrystalline graphitic carbon and boron nitride. The ball-milled mixture is encapsulated and sintered at a pressure of about 5-25 GPa and at a temperature of about 1000-2500 K.

The invention is also a bulk, superhard nanocomposite compact prepared by the process of ball-milling a mixture of graphite and hexagonal boron nitride until the mixture is transformed into amorphous and/or nanocrystalline graphitic carbon and boron nitride. The ball milled mixture is encapsulated and sintered at a pressure of about 5-25 GPa and at a temperature of about 1000-2500 K.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and form a part of the specification, illustrate the embodiment(s) of the present invention and, together with the description, serve to explain the principles of the invention. In the drawings:

Figure 1 shows a high magnification SEM image of the precursor material used to prepare the bulk, superhard nanocomposite compact of the invention;

Figure 2 shows an x-ray diffraction pattern of the precursor material of Fig. 1;

Figure 3 shows and a Raman spectrum of the precursor material of Fig. 1;

Figure 4 shows diffraction patterns plotted as intensity versus 2-Theta Angle;

Figure 5 shows synchrotron x-ray patterns in the energy dispersive mode for three compacts of the invention;

5 Figure 6 shows a synchrotron XRD pattern plotted as intensity versus d-spacing for a compact of the invention prepared at 20 GPa and 1900 C;

Figure 7 shows a high-resolution transmission electron microscopy (HRTEM) image of a compact of the invention; and

10 Figure 8 shows an electron energy-loss spectroscopy (EELS) spectrum for amorphous, ball-milled starting material and an EELS spectrum for a compact of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention includes a superhard B-C-N nanocomposite compact and a method for preparing the compact. The compact includes nanocrystalline 15 grains of at least one high-pressure B-C-N phase embedded in a diamond-like amorphous matrix. The practice of the invention can be further understood with the accompanying figures. Similar or identical structure is identified using identical callouts.

20 The compact is produced by first preparing a ball-milled mixture of graphite and hexagonal boron nitride (hBN). A tungsten carbide vial and tungsten carbide milling balls were used for the ball milling procedure. Figure 1 shows a high magnification scanning electron microscope (SEM) image of the ball-milled 25 powdered mixture after 34 hours of ball milling. As the SEM image shows, the mixture is dark, has a grain size less than 0.1 micron, and does not appear to have a crystalline morphology.

Figure 2 includes two x-ray diffraction spectra. The upper spectrum is of the mixture of graphite and hexagonal boron nitride before ball milling. The lower spectrum is of the ball-milled mixture after 34 hours of ball milling. As Fig. 2 shows, the ball-milled mixture appears to be amorphous.

Figure 3 shows three Raman spectra. The upper spectrum is of hexagonal boron nitride (hBN), the middle spectrum is of graphite, and the lower spectrum is of the ball-milled mixture of graphite and hBN. The lower spectrum includes a peak at 1350 cm^{-1} (a defect/disorder peak) and a peak at 1580 cm^{-1} that is assigned to a graphitic phase. Importantly, the lower spectrum suggests that along with a graphite phase, the ball-milled mixture also includes grains of nanocrystalline particles and the intensity ratio between the 1350 cm^{-1} peak and the 1580 cm^{-1} peak indicates that the grain size is about 2-3 nanometers (nm).

A sample of the ball-milled powder having the lower Raman spectrum of Fig. 3 was encapsulated in a cylindrical platinum capsule and compressed using a multi-anvil to a pressure of about 5-25 GPa. At this elevated pressure, the encapsulated powder was sintered at a temperature of about 1000-2500 K for 2-120 minutes. After the sintering period, the capsule was brought to room temperature and decompressed to ambient pressure. The compact was removed from the capsule and the ends of the compact were polished with a diamond abrasive. The resulting polished compact was a well-sintered cylindrical bulk compact having a height of about 1.5-mm and a diameter of about 1.2-mm. These dimensions are a reflection of the dimensions of the capsule used. Obviously, compacts of different sizes and shapes depend on the size and shape of the capsule and the cell assembly used. A larger capsule and cell assembly would require a larger sample size and result in a larger compact. Likewise, smaller capsules and cell assemblies could also be used to prepare smaller compacts.

Several examples of the bulk compact of the invention were prepared according to the conditions summarized in Table 1 below.

TABLE 1

Entry	Precursor powder composition	Pressure (GPa)	Sintering temperature (K)	Sintering Time (minutes)	Vickers hardness (GPa)	Color
1	BCN	20	1300	2		Black
2	BCN	20	2100-2400	10		Light yellow
3	BC ₂ N	6-8	1500	120		Black
4	BC ₂ N	10	2000	5		Black
5	BC ₂ N	15	1800	5	50	
6	BC ₂ N	15	2000	5	41	Black
7	BC ₂ N	16	2100	5	50	Gray-white
8	BC ₂ N	20	2200	5	62	Light yellow
9	BC ₂ N	25	2130	10		Light yellow
10	BC ₂ N	25	2300	60		Light yellow
11	BC ₄ N	20	2300	5	68	brown

As Table 1 shows, the compacts varied in color. Some were translucent, while
5 others were opaque. Some were black (entries 1, 3, 4, and 6) while others were
gray-white (entry 7), brown (entry 11), and light yellow (entries 2, 8, 9, and 10).
The color seems to be dependent on the relative amount of graphite, the pressure,
and the sintering temperature).

The Vickers hardness for several of them (entries 5, 6, 7, 8, and 11) were
10 measured and determined to be in the range of about 41-68 GPa. The Hv for any
particular compact of the invention appears to be dependent upon the precise
composition of the precursor powder and on the synthesis conditions. Three
precursor powder compositions were used. Entries 1 and 2 (BCN) employed a
composition of a 1:1 molar ratio of graphite:hBN (i.e. 1 part graphite and 1 part
15 hBN). Entries 2-9 (BC₂N) employed a composition 2:1 molar ratio of graphite:hBN
(i.e. 2 parts graphite and 1 part hBN). Entry 11 (BC₄N) employed a powder
composition of a 4:1 molar ratio of graphite:hBN (i.e. 4 parts graphite and 1 part

hBN. Pressures varied from about 6 GPa to about 25 GPa, sintering temperatures varied from about 1300 K (entry 1) to about 2400 K (entry 2), and sintering times varied from 2 minutes (entry 1) to about 120 minutes (entry 3). The preparation of several of these compacts is now described.

5

EXAMPLE 1

The compact of entry 2 was synthesized as follows. About 5 grams of a ball milled mixture of a 1:1 molar ratio of graphite:hBN were prepared. About 3 mm³ of the ball-milled mixture was placed into a platinum capsule. Using a split-sphere multi-anvil press, the encapsulated mixture was subjected to a pressure of about 20 GPa and then sintered at a temperature of about 2100-2400 K for about 10 minutes. The resulting compact was light yellow in color.

10

EXAMPLE 2

The compact of entry 5 was synthesized as follows. About 3 mm³ of the ball-milled mixture described in Example 1 was placed into a platinum capsule. 15 Using the anvil press of example 1, the encapsulated mixture was subjected to a pressure of about 15 GPa, and then sintered at a temperature of about 2100 K for about 5 minutes. The resulting bulk compact had a measured Vickers hardness was 50 GPa.

15

EXAMPLE 3

The compact of entry 8 was synthesized as follows. About 3 mm³ of the ball-milled mixture described in Example 1 was placed into a platinum capsule. 20 Using the anvil press of Example 1, the encapsulated mixture was subjected to a pressure of about 20 GPa, and then sintered at a temperature of about 2200 K for about 5 minutes. The resulting bulk compact of the invention was light yellowish in color, translucent, and had a measured Vickers hardness of 62 GPa.

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EXAMPLE 4

The compact of entry 9 was synthesized as follows. About 3 mm³ of the ball-milled mixture described in Example 1 was placed into a platinum capsule. 25 Using the anvil press of Example 1, the encapsulated mixture was subjected to a

pressure of about 25 GPa, and sintered at a temperature of about 2130 K for about 10 minutes. The resulting bulk compact of the invention was light yellow in color.

EXAMPLE 5

5 The compact of entry 10 was synthesized as follows. About 3 mm³ of the ball-milled mixture described in Example 1 was placed into a platinum capsule. Using the anvil press of Example 1, the encapsulated mixture was subjected to a pressure of about 25 GPa, and sintered at a temperature of about 2300 K for about 60 minutes. The resulting bulk compact of the invention was light yellow in
10 color.

EXAMPLE 6

Compact number 11 was synthesized as follows. A mixture of a 4:1 molar ratio of graphite:hBN was prepared. About 3 mm³ of the ball-milled mixture was placed into a platinum capsule. Using the anvil press of Example 1, the
15 encapsulated mixture was subjected to a pressure of about 20 GPa and sintered at a temperature of about 2200 K for about 5 minutes. The resulting bulk compact of the invention was brownish and translucent, with a measured Vickers hardness was 68 GPa.

The microstructure and composition of the compact of the invention was
20 probed using a variety of techniques. While optical microscopy and scanning microscopy were relatively uninformative, the granular structure of the compact of the invention was revealed using the Advanced Photon Source (APS) at Argonne National Laboratory, which provided monochromatic synchrotron x-ray diffraction in angle dispersive mode. The compact was interrogated using a narrow (5 x 7
25 μm^2), collimated X-ray beam ($\lambda=0.4146 \text{ \AA}$). The x-rays by the compact were collected using an image plate in angle-dispersive mode to cover a 2-Theta (2Θ) angle range up to 32 degrees, which corresponds to a minimum d-spacing of 0.77 \AA . Changing the position of the beam spot on the compact had no effect on the

diffraction pattern, which indicated that the sample was homogeneous in structure and composition.

Figure 4 shows X-ray diffraction patterns that are plotted as intensity versus 2-Theta Angle for the BC₂N bulk compact of the invention synthesized at a pressure 20 GPa and a sintering temperature of 2200 K. The upper diffraction pattern was obtained when the compact was rocked with an amplitude of 5 μ m. The middle diffraction pattern is for the non-rocking, stationary compact, and the lower pattern is a standard diffraction pattern of cerium oxide (CeO₂), which is included in order to indicate the resolution of the x-ray diffraction instrument. As Fig. 4 shows, the peaks of the middle pattern are about 5-6 times as broad as the peaks of the lower pattern. As the upper pattern shows, the peaks broadened even more (8-10 times as broad as the lower pattern) when the sample was rocked. From these observations, it was concluded that the compact includes nanocrystalline grains. Using Scherrer's equation, the grain size was estimated at about 4-8 nm.

The major diffraction peaks shown in Fig. 4 for the compact of the invention are consistent with a face-centered-cubic (fcc) zinc-blende (ZnS) structure with a unit cell parameter $a=3.595(7)$ \AA . This unit cell dimension lies between diamond ($a=3.567$ \AA) and cBN ($a=3.616$ \AA), and is in close agreement with the unit cell parameter reported by E. Knittle et al. in "High Pressure Synthesis, Characterization, and Equation of State of Cubic C-BN Solid Solutions," Phys. Rev. B. vol. 51, 1995, pp. 12149-12156; by T. Komatsu et al. in "Creation of Superhard B-C-N Heterodiamond Using Shock Wave Compression Technology," J. Mater. Processing Technology, vol. 85, 1999, pp. 69-73; and by W. Utsumi et al., in "In situ X-Ray and TEM Observations on the Phase Transitions of BC₂N Under Static Pressures," Proceedings of AIRAPT-18, Beijing, 2001, p. 186. From these papers, it appears that E. Knittle et al., T. Komatsu et al. and W. Utsumi et al. were unable to produce the well-sintered, bulk superhard nanocomposite compact of the present invention.

Figure 5 shows synchrotron x-ray diffraction patterns in the energy dispersive mode for three compacts of the present invention. The compact that produced the top x-ray diffraction pattern was sintered at 15 GPa and 2000 K. The compact that produced the middle x-ray diffraction pattern was sintered at 16 GPa and 2100 K. The compact that produced the bottom x-ray diffraction pattern was sintered at 20 GPa and 2200 K. Each pattern includes the $<111>$ pc and $<220>$ pc peaks of the fcc lattice. Compacts of the invention prepared at 20 GPa were about 15-20% harder than those prepared at 15-16 GPa. Compacts that were prepared at still lower pressures produced x-ray diffraction patterns that exhibited additional peaks and apparent peak splitting that was most noticeable for the $<200>$ pc peak. This may suggest the existence of a superlattice, lower symmetry, or an additional phase. Generally, compacts prepared at higher pressures appear to have higher symmetry.

Figure 6 shows the synchrotron XRD pattern, plotted as intensity in arbitrary units versus d-spacing in angstroms, of a compact prepared at 20 GPa and 2200 K. The top left inset shows that the $<111>$ peak can be fitted by a sum of two curves; a broadened crystalline peak (curve A) and an amorphous hump (curve B). The plus (+) indicates the data observed and the dark solid line is the curve calculated from the fitting of curve A with curve B.

Figure 7 shows high-resolution transmission electron microscopy (HRTEM) image of a BC₂N compact of the present invention synthesized at a pressure of 20 GPa and a sintered at a temperature of 2200 K for 5 minutes. The HRTEM image confirms the presence of 3-8 nm nanocrystalline grains with an average size of about 5 nm, which is consistent with the synchrotron X-ray diffraction pattern. The zinc-blende fcc structure, apparent from Fig. 4, is confirmed by the electron diffraction pattern shown in the top right inset of Fig. 7. Figure 7 includes an enlarged image of a grain. The enlarged image appears to include an apex of a regular icosohedron, a regular polyhedron with 20 triangular faces and five-fold symmetry. Lines have been added to more clearly show these features. Also

according to Figure 7, the grain boundaries between the nanocrystalline grains appear to be amorphous.

The chemical composition and chemical bonding of individual grains of the compact were determined using electron energy-loss spectroscopy (EELS), a 5 powerful technique for obtaining local chemical composition and chemical bonding information in materials composed of light elements. Samples of the compact were prepared for EELS by an ion-thinning process or by directly impacting the sample into fine powder. The results were the same for both sample preparation methods. A narrow (3-4 nm) focused electron beam was used to probe the 10 chemical composition and bonding of individual nanocrystalline grains. Figure 8 shows an upper EELS spectrum for the amorphous, ball-milled starting material and a lower EELS spectrum for a single nanocrystalline grain. The lower EELS spectrum includes the K-edges for B, C, and N, which confirms that the grain is composed of a single ternary B-C-N phase rather than a mixture of a diamond 15 phase and a cBN phase. The upper EELS spectrum for the amorphous ball-milled starting material includes π^* peaks at the K-edges for the B, C, and N. The appearance of these π^* peaks in the amorphous starting material suggests the presence of sp²-hybridized hexagonal ring fragments. The π^* peaks of the EELS spectrum of the amorphous material do not appear in the EELS spectrum of the 20 compact.

The chemical composition of the grain boundaries was examined using a combination of HRTEM and EELS. Unexpectedly, the grain boundaries are composed of amorphous, diamond-like carbon (DLC). DLC is typically produced by such methods as vacuum arc or pulsed laser deposition, and has stimulated 25 great interest because of its high hardness, chemical inertness, thermal stability, wide optical gap, and negative electron affinity. It is believed that the bulk, superhard, nanocomposite compact of the invention is the first bulk, nanostructured compact reported with DLC grain boundaries, which are believed to contribute significantly to the mechanical strength of the compact.

The enhanced fracture toughness of the compact of the invention is likely due, at least in part, to the substantial absence of vacancies and dislocations in the individual nanocrystalline grains, and also to the difficulty of microcrack propagation through the amorphous grain boundaries separating the grains.

5 The effects of using a ball-milled amorphous material as the precursor material were examined by preparing compacts from a different precursor material: a mixture of graphite and hexagonal boron nitride (hBN) that had not been subjected to ball milling. Compacts prepared without ball milling the mixture of graphite and hBN did not include nanocrystalline grains of BC₂N. Instead, these
10 compacts included segregated phases of diamond and cBN. The presence of segregated phases was first suggested by optical microscopy, more strongly indicated by x-ray diffraction spectra that showed twin-peaks of all the major x-ray diffraction peaks, and finally confirmed by Raman spectra that showed the characteristic peaks of diamond and cBN.

15 The invention also includes machining tools of the bulk superhard compact of the invention. The compact could be used for drilling, cutting, puncturing, and other types of machining.

In summary, the invention includes a well-sintered, bulk, superhard, nanocomposite compact and a method for preparing the bulk compact. The bulk
20 compact includes nanocrystalline grains of at least one high-pressure phase of B-C-N embedded in a diamond-like amorphous carbon matrix. A variety of analytical techniques show that the bulk compact contains nanocrystalline grains of B-C-N having a diamond-like structure. The structure symmetry and Vickers hardness (Hv = 50-73 GPa) of the bulk compact of the invention appear to
25 increase with the pressure used to prepare the compact. The Vickers hardness of several examples of the bulk compact was higher than that for cBN (47 GPa, see T. Taniguchi et al. in "Sintering of cubic boron nitride without additives at 7.7 GPa and above 2000 °C, J. Mater. Res., vol. 14, pp. 162-169, 1999) and for hBN single crystals (45-50 GPa, see Handbook of Ceramic Hard Materials, R. Riedel ed., pp.

104-139, Wiley-VCH Verlag GmbH, D-69469, Weinheim, 2000) and were very close to the hardness of diamond (70-100 GPa). It is expected that the compact of the invention is more stable at high temperatures than diamond and that machining tools employing the compact of the invention will not react with ferrous metals during high-speed cutting.

5 The foregoing description of the invention has been presented for purposes of illustration and description and is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching. Commercially available autofocus laser end effectors, for example, could be used instead of the laser end effectors described herein.

10 The embodiment(s) were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilize the invention in various embodiments and with 15 various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.